

Peculiarities of Thermoelastic Martensitic Transformation in the Cu-Zn-Al and Cu-Zn-Al-V after Decomposition of the β -Solid Solution

V. Zel'dovich, I. Khomsкая, N. Frolova and T.V. Novoselova

Institute of Metal Physics, 18 S. Kovalevskaya Str., 620219 Ekaterinburg, GSP-170, Russia

Abstract. Dilatometric, metallographic, and electron-microscopic methods were used to study martensitic transformations in Cu-Zn-Al alloys that were subjected to a heat treatment to the decomposition of β solid solution at temperatures of α -phase precipitation (635-530°C) and bainite formation (300-125 °C). The partial decomposition and the accompanying redistribution of the components were shown to alter the type of martensitic transformation from nonthermoelastic to thermoelastic with a corresponding change in the martensite morphology from plate type to needle type (spear-shaped). A decrease in the temperature of isothermal anneal in the $\alpha+\beta$ range from 600 to 530°C substantially decrease the M_s temperature (by 140 °C). The temperature hysteresis of the transformation changes from 0 to 70 K.

1. INTRODUCTION

The decomposition of the supersaturated solid solution based on the β phase and the bainitic transformation in Cu-Zn-Al alloys have been studied in many works [1-5]. However, the effect of these processes on subsequent martensitic transformation is still poorly understood [1].

This paper aims to study the temperature range and type of martensitic transformation and the martensite structure in the Cu-Zn-Al alloys in which decomposition of the β solid solution occurred.

2. EXPERIMENTAL PROCEDURE

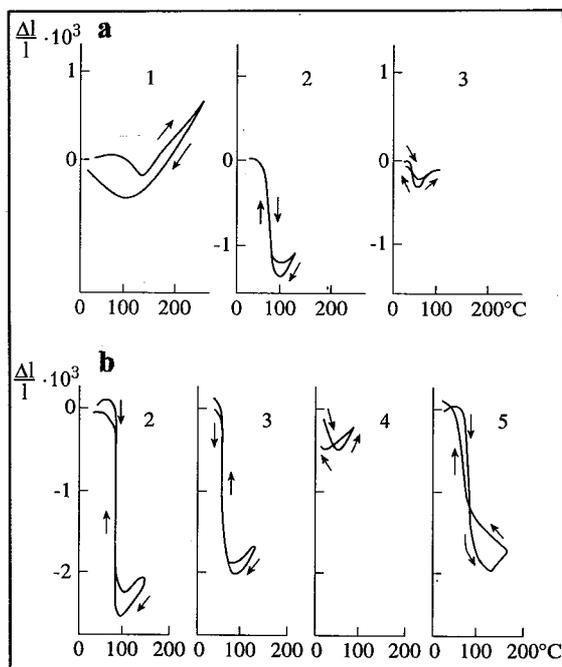
The Cu-Zn-Al alloys containing (wt%) 77,1 Cu, 16,7 Zn and 6,2 Al (alloy 1), 76,5 Cu, 16,7 Zn and 6,8 Al (alloy 2) and 75,2 Cu, 18,4 Zn, 6,3 Al, 0,1V (alloy 3) were produced from pure metals in a vacuum induction furnace. Homogenization annealing was performed at temperatures of 910-850 °C, corresponding to the single-phase β field. Subsequent treatment was performed by different schedules. Dilatometric measurements were performed in a Chevenard dilatometer using differential registration.

The transformation temperature range was determined with an accuracy of 5 K, and the relative change in the specimen length was measured with an accuracy of $\pm 0.01\%$. Thin foils for electron-microscopic examination in a JEM-200CX electron microscope were prepared from the alloy 1 specimen preliminary used for metallographic analysis.

3. DILATOMETRIC ANALYSIS

Upon cooling from 900°C, a substantial elongation of the specimen of alloy 1 is observed at 650-480°C due to the α -phase precipitation. Upon further cooling, no bends are observed in the cooling curve. Cooling from 20 to -196°C also does not cause martensitic transformation. The dilatometric analysis indicated that the martensitic transformation in alloy 1 and 2 after quenching are of the non-thermoelastic type. Because no martensitic transformation occurs after a slow (8°C/min) cooling from the single-phase β field, it was of interest to study the effect of incomplete β -phase decomposition on the temperatures of

subsequent martensitic transformation. To this end, the specimens of alloys 1 and 2 were heated to the β field and cooled to temperatures of the two-phase $\alpha+\beta$ field (635-530°C) or to 125°C, held for 60 or 15 min, and cooled to room temperature. The data obtained are shown in Fig. 1 and in the table 1. It is



β field and the temperature of holding (T_h) in the ($\alpha+\beta$) field on the M_s temperature in the Cu-Zn-Al alloys

Alloy	$V_{cool.}, ^\circ C/min$	$T_h, ^\circ C$	$M_s, ^\circ C$
1	8	635	110
	8	600	100
	8	560	55
	50	560	50
	50	530	-30
	50	125	5 (1cycles) -100(2) -115(3-4)
2	8	600	100
	8	565	90
	50	550	25
	50	530	20
	50	125	80

Table 1

Effects of the rate of cooling (V_{cool}) from the

Figure 1: Dilatometric curves of the martensitic transformations in alloys (a) 1 and (b) 2 after holding at (1) 635; (2) 600; (3) 560; (4) 550 and (5) 125°C.

seen that all the specimens undergo martensitic transformation upon cooling after various isothermal holdings. The shapes of the dilatometric curves of alloy 1 preliminary held at 635 °C (Fig.1a, curves 1) show signs of thermoelastic martensitic transformation. A decrease of the holding temperature (T_h) from 635 to 600 °C changes the shape of dilatometric curves (Fig.1, curves 2). In addition, the temperature hysteresis of transformation decreases to zero. As the cycles are repeated (three cycles), the positions of the temperature range of the transformations, the shapes of the curves, and the value of the dilatometric effect remain unaltered. A decrease of T_h to 560°C substantially decreases the M_s temperature (to 50°C), decreases the value of the dilatometric effects, but does not change the type of the transformation (Fig.1a, curves 3,2). A further decrease of T_h from 560 to 530°C leads to a further decrease in M_s (to -30°C). The transformation remains thermoelastic, but the hysteresis substantially (to 70°C) increases. A low-temperature treatment (125°C, 15 min) leads to a further substantial decrease in M_s (to -100°C after two cycles, see the table 1).

All of the above signs of thermoelastic transformation observed in alloy 1 are also characteristic of alloy 2 after the same treatment (compare Fig.2a, 2b). As in alloy 1, the M_s temperature in alloy 2 decreases with decreasing temperature of isothermal holding in the two-phase $\alpha+\beta$ field from 600 to 530°C. This occurs

due to a higher enrichment of the retained β phase in zinc [2]. Thus, the martensitic transformation in the alloys under study becomes thermoelastic due to a partial decomposition of the β solid solution and the corresponding redistribution of the alloy components.

The martensitic transformation in alloy 3 after quenching is of the thermoelastic type. The dilatometric curves of the martensitic transformations in alloy 3 after various heat-treatment are shown in Fig.2. The values of the martensitic transformations temperatures and dilatometric effects are shown in the table 2.

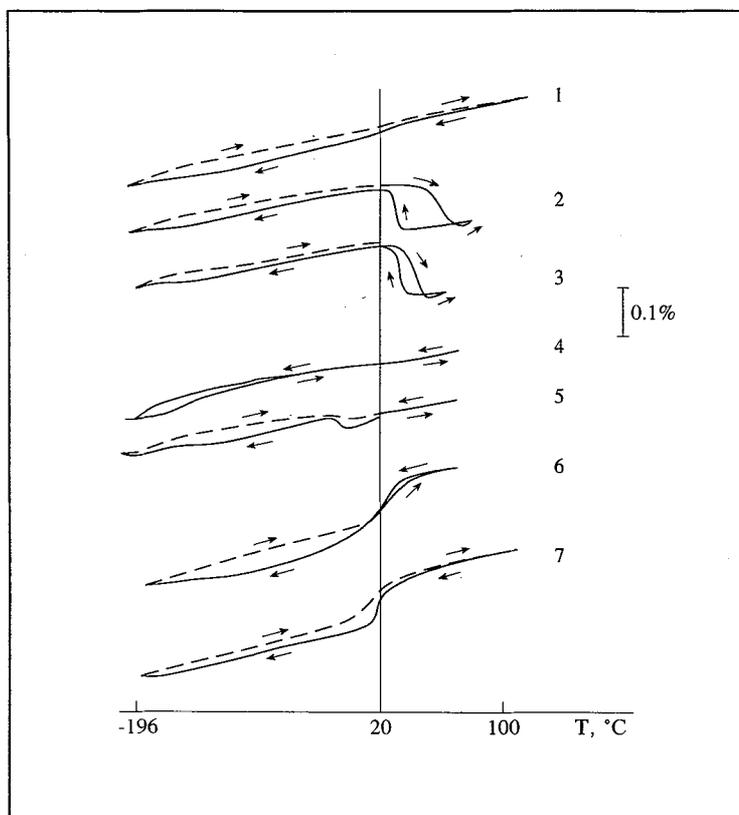


Figure 2: Dilatometric curves of the martensitic transformations in alloy 3 after quenching (1), holding at (2,3) 550°C, 3h (2-first, 3-second cycle); (4) 510°C, 40 min; (5) 510°C, 3h; (6) 200°C, 2h; (7) 165°C, 30 min.

Table 2

Effects of the temperature (T_h) and time (τ) holding in ($\alpha+\beta$)-field on the temperatures and dilatometric effects of the martensitic transformations in alloy 3.

$T_h, ^\circ\text{C}$	τ, min	$M_s, ^\circ\text{C}$	$M_f, ^\circ\text{C}$	$\Delta l/l, \%$	$A_s, ^\circ\text{C}$	$A_f, ^\circ\text{C}$	$\Delta l/l, \%$	$\Delta T_{50}, ^\circ\text{C}$
550	180	40	20	0,12	40	75	-0,12	27
510	40	-170	-185	-0,04	-175	-150	0,04	15
	180	-15	-35	0,03	-35	-15	-0,03	0
200	40	-160	-185	0	-185	-165	0	0
	120	40	-30	-0,07	-10	40	0,08	10
165	30	40	15	-0,08	15	45	0,09	3
	30	45	-5	-0,08	0	40	0,1	0

It is seen, that bainitic transformation change a sign of the dilatometric effects of the following martensitic transformation. During martensitic transformation the length of specimens increased after decomposition in the range 500-600°C whereas the one decreased after bainitic transformation.

4. METALLOGRAPHIC INVESTIGATION

The microstructure of the as-cast alloy 1 consists of light α -phase crystals and dark-etched zinc-rich β matrix. The absence of martensite in the as-cast β phase indicates a substantial enrichment of β phase in zinc and a resulting decrease in the martensitic point. After heating to 880°C and water quenching, the alloys contain martensite (Fig. 3a). The martensite structure consists of crystals of two types: extended plate-type crystals with an internal structure and spear-shaped crystals. The former crystals dominate in the structure.

The microstructure of alloy 1 after holding at 560°C and water quenching is shown in Fig. 3b.

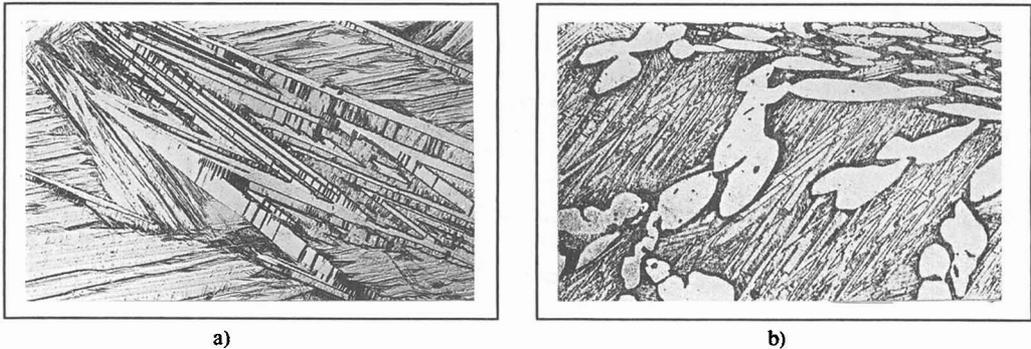


Figure 3: (a) Microstructure of alloy 1 (a) quenched from 880°C ; (b) after holding at 560°C. (x620).

A partial decomposition of the β phase occurs upon holding at 560°C, according to the dilatometric data. The α -phase crystals precipitate at grain boundaries and inside the β grains along one to four directions. These crystals are shaped as rods of parallelogram or polygonal cross section. The untransformed zinc-rich regions of the β phase undergo martensitic transformations upon subsequent cooling (Fig. 1a, curve 3). The martensite forms predominantly as spear-shaped crystals (Fig. 3b). The fact that the martensitic transformation becomes thermoelastic is indicated by the shape of the dilatometric curves (Fig. 1, curves 3) and by the appearance and disappearance of a relief at the surface of metallographic specimens. Thus, the predominantly spear-shaped martensite crystals are associated with the thermoelastic martensitic transformation.

It is known [5] that a low-temperature holding at 150°C may substantially decrease the temperature range of martensitic transformation in the Cu-Zn-Al alloys. Two types of crystals formed due to the decomposition of the β phase are observed, and no martensite is found in the microstructure of alloy 1 alloys after cooling from the β field to 125°C, holding and subsequent water quenching. Cooling in the upper temperature range (600-500°C) of the α + β field leads to the formation of a Widmanstatten structure containing rodlike α -phase crystals. Upon further cooling, the retained regions of the β phase undergo a low-temperature decomposition at 300-125°C with the formation of fine plate-type bainite crystals. The absence of martensite is caused by a substantial enrichment of small untransformed β -phase regions in zinc and by a resulting substantial decrease of M_s (see the table 1).

The temperature of martensitic transformation in the Cu-Zn-Al alloy is known to be very sensitive to chemical composition [2]. In the alloys under study, this dependence is most pronounced after low-temperature holding at 125°C (see the table 1). The microstructure of alloy 2 (Fig. 4) differs from that of alloy 1 after the same treatment. A small amount of fine α -phase crystals precipitated predominantly at some boundaries of the initial β -phase grain and a small amount of plate-type bainite crystals is observed in alloy 2. The bainite crystals are often coupled, forming butterfly type arrangements. The main volume of the former β grains is occupied by extended plate-type martensite crystals (Fig. 4). The aluminum content in alloy 2 is

somewhat higher than that in alloy 1 (6.8 and 6.2 wt %, respectively). This relatively small increase in aluminum content seems to be sufficient to substantially deplete the β phase of zinc and, correspondingly, to significantly elevate (by 75°C) the martensitic point after holding at 125°C (see the table 1).

5. ELECTRON-MICROSCOPIC EXAMINATION

As was shown by the metallographic study, martensite crystals of two morphologies (plate-type and spear-shaped) are present in the alloys under study after water quenching. The internal structure of the extended plate-type martensite crystals is shown in Fig.5. It is seen that the martensite crystal is divided into

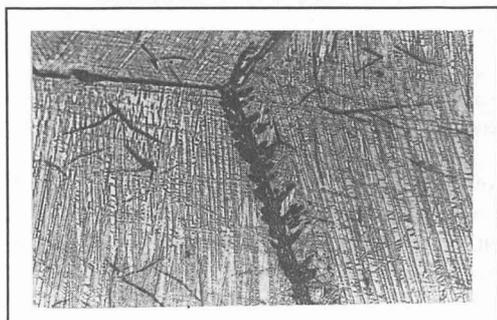


Figure 4: Microstructure of alloy 2 after cooling at a rate of $\sim 50^\circ\text{C}/\text{min}$ and holding at 125°C ($\times 620$).

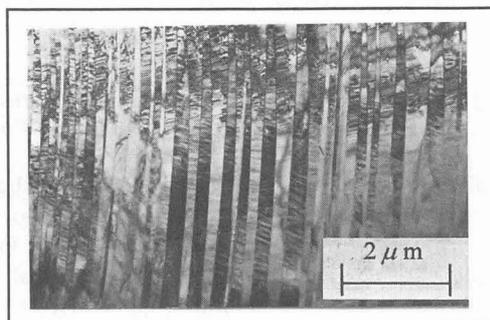


Figure 5: Internal structure of the extended plate-type martensite crystals after quenching from 880°C .

alternating plates with a fine banded structure (substructure). The band direction as well as the crystallographic orientation of the plates alternates. Using electron diffraction analysis and dark-field images, we found that these internal plates are twinned to one another, and the twinning plane is the $\{111\}_{\beta_2}$ plane. It should be noted that the alloys under study are related to the β -brass type alloys, in which the ordering rate is high to an extent that this process cannot be suppressed even upon rapid quenching [4,6]. Analyzing diffraction patterns and dark-field image micrographs, we found also that the homogeneous ordering and a network of isotropic wavy antiphase domain boundaries in our alloys were completely retained in the martensite phase, i.e., the microstructure of the ordered martensite inherits the superstructure of the ordered β_2 phase of the CsCl (B2) type [6].

As was shown by metallographic examination, the microstructure of the alloys water quenched from 600 and 560°C , i.e., from the temperatures of the two-phase $\alpha+\beta$ field consists of rod-type α -phase crystals and needle-type (spear-shaped) martensite crystals (Fig.3b). Electron microscopy indicates that, in addition to these phases, regions of the ordered β_2 phase that did not transform to martensite are present in alloy 1 after holding at 560°C . Figure 6a displays a spear-shaped crystal of thermoelastic martensite. The crystal consists of two parts (denoted by 1 and 2) in which a fine banded structure (substructure) of one-two orientations is observed. The fine structure of these spear-shaped crystals appears at the instant they form and results from the transformation [6]. As was shown by electron diffraction and dark-field images, the two parts of the spear-shaped β'_2 - martensite crystal (Fig.6a) are twinned to each other, and the twinning plane is the $(121)_{\beta'_2}$ plane.

We now consider the microstructure of alloy 1 after cooling from the single-phase β field at a rate of $\sim 50^\circ\text{C}/\text{min}$ to 125°C , holding for 15 min, and water quenching. Metallographic examination of this alloy indicates the presence of two phases: rodlike α -phase crystals and fine spear-shaped bainite crystals). In addition, electron-microscopy of this alloy indicates that fine plate-type martensite crystals (2) of two orientations grow from the bainite crystals (1 in Fig.6b).

In addition, this specimen was subjected to two cycles of cooling to -180°C and warming to $\sim 20^\circ\text{C}$ in the column of the electron microscope. The thermoelastic migration of the interface between a martensite crystal and the matrix was traced. Upon cooling, the martensite crystal having a twinned internal structure laterally grows into the neighboring crystal with the structure of the matrix β_2

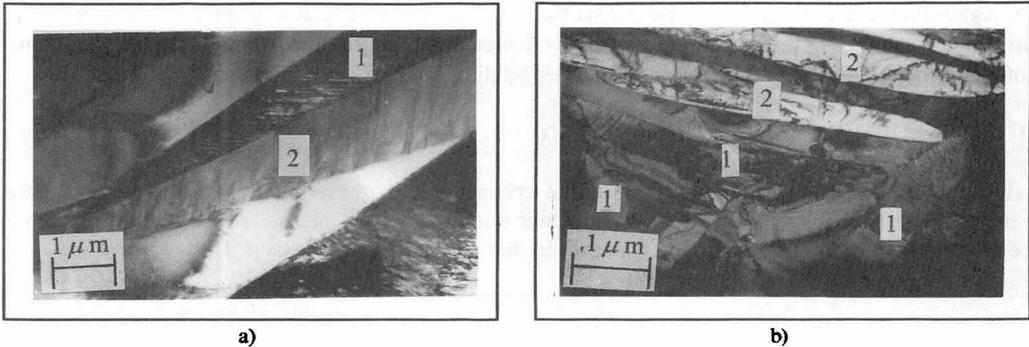


Figure 6: (a) A spear-shaped crystal of thermoelastic β'_2 martensite and (b) crystals of (1) bainite and (2) martensite in alloy 1 after holding at (a) 560°C and (b) 125°C and cooling.

phase. As the temperature decreases to $\sim -180^\circ\text{C}$, the growth stops. On cooling, the boundary of the martensite crystal travels a distance equal to the width of the neighboring crystal. Upon heating to $\sim -80^\circ\text{C}$, the boundary travels in the reverse direction, i.e., the martensite crystal is contracted and returns to its original position at a temperature of about 0°C . Note that the boundary between the martensite crystal and the matrix is stepwise during the motion. Supposedly, this is caused by a local stress concentration at the interphase interface. This stress concentration is considered [7] to be the factor responsible for the increased mobility of the phase boundary.

6. CONCLUSION

(1) In the Cu-Zn-Al alloys studied, a partial decomposition of the β solid solution and the related redistribution of the components change the type of martensitic transformation from non-thermoelastic to thermoelastic.

(2) The change of the type of martensitic transformation from non-thermoelastic to thermoelastic corresponds to a change in the martensite morphology from predominantly plate-type to spear-shaped.

(3) The redistribution of components upon isothermal holding at temperatures of the $\alpha+\beta$ field substantially (by 80-140°C) decreases the start temperature of martensitic transformation.

References

- [1]. Otsuka K., Shimizu K., Suzuki Y., Sekiguchi Y., Tadaki C., Honma T., and Miyazaki S., *Shape Memory Alloys* (Hiroyasu Funakubo, 1984).
- [2]. Delaey, L. and De Vos R., *Z. Metallkd.*, **70**, (1979) 33-37.
- [3]. Takezawa K., and Sato S., *Mater. Trans. JIM*, **31** (1991) 766-773.
- [4]. Wu M.N., Perkins J. and Wayman C.M., *Acta Metall.*, **37** (1989) 1821-1837.
- [5]. Hamada K., Wu M.N. and Wayman C.M., *Mater. Trans., JIM*, **32** (1991) 747-756.
- [6]. Warlimont H. and Delaey L., *Martensitic Transformations in Copper, Silver, and Gold-Based Alloys*, Oxford: Pergamon, 1974.
- [7]. Shimizu K and Otsuka K., *Shape Memory Effects in Alloys*, Perkins, J., Ed. (New York: Plenum, 1975) 60-87.